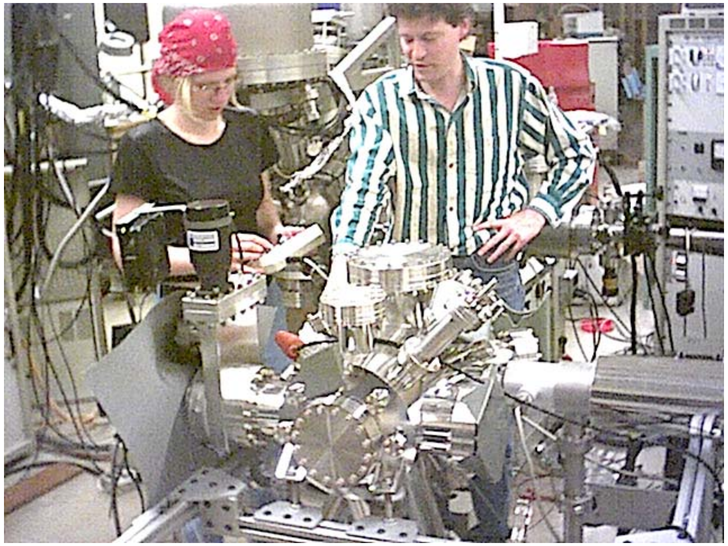
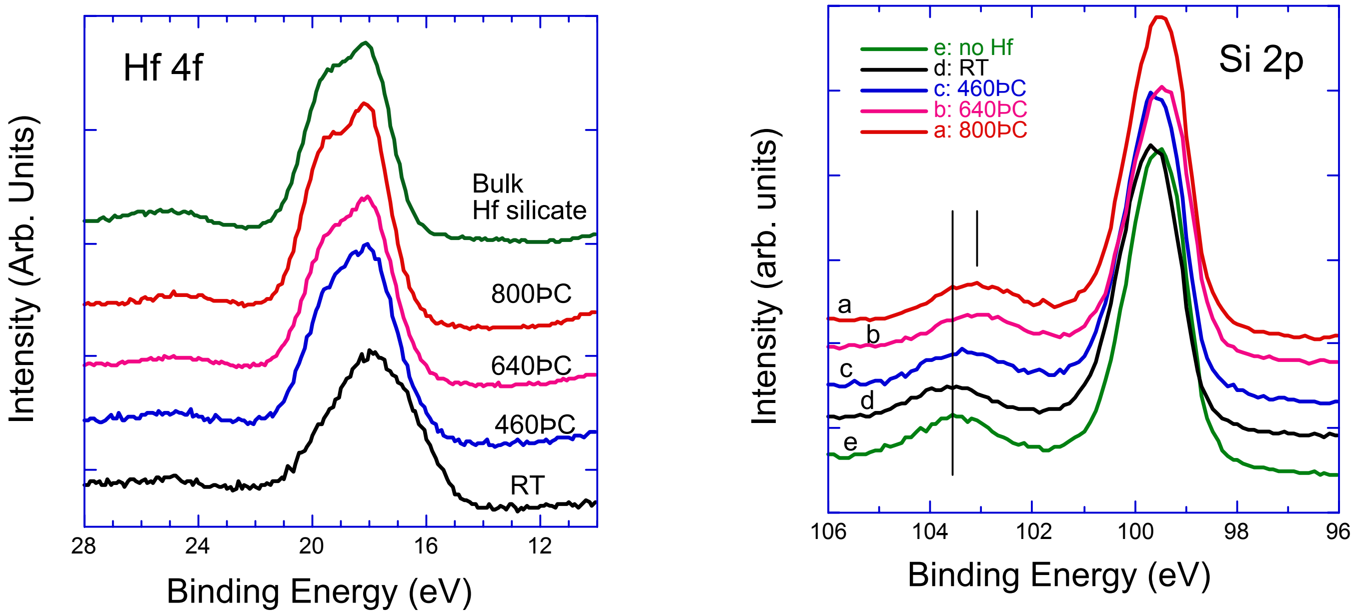


Paul F. Lyman, Univ. of Wisconsin-Milwaukee DMR-9984442

Paul Lyman shows Anna Brinck how to adjust a RHEED pattern. Anna participated as a Undergraduate Research Assistant and REU student from 1999 to 2002, and is a co-author on two publications. Susa Stone (REU) and Daniel Shillinglaw (Research Assistant) are two other undergraduates who worked successfully on this project. All students learned how to use modern laboratory instrumentation, acquired and analyzed data, and presented their findings. Two graduate students, Trevor Johnson-Steigelman and Swapnil Tripathi, are also involved in this effort.

Formation of Hafnium Silicate by Solid-State Reaction



Evolution of Hf and Si x-ray photoelectron spectroscopy (XPS) signals as Hf metal is reacted with SiO_2 to form a hafnium silicate compound.

Paul Lyman DMR-9984442

At the University of Wisconsin-Milwaukee, Asst. Prof. Paul Lyman and his research group have been examining new processing routes to the formation of novel dielectric compounds. A new generation of insulating materials (having a higher dielectric constant than silicon dioxide) will be needed by the microelectronics industry by 2006 to enable continued miniaturization of IC's, with the resultant performance and cost improvements. Hafnium silicate is a potential replacement for silicon dioxide, but questions remain about its compatibility with conventional processing and its stability.

A thin film of Hf metal was deposited on a conventional SiO2 layer, and then annealed to induce a solid-state reaction. The left panel shows the evolution of the Hf 4*f* corelevel lineshape and binding energy (BE) upon annealing; after the film is reacted at 800˚C, the feature coincides with that of a bulk Hf silicate standard. This provides strong evidence for formation of Hf silicate by solid-state reaction.

The right panel shows the development of the Si 2*p* corelevel during the same reaction sequence. Of particular importance is the position of the feature at deeper BE (~103.5 eV) that corresponds to oxidized Si (Si^{-4}). As the film reacts, the oxide feature shifts continuously to shallower BE, eventually shifting by more than 0.5 eV. In both SiO_2 and Hf silicate, each Si atom resides at the center of a tetrahedron, surrounded by four O neighbors, explaining the rough similarity of the Si BE position for SiO_2 and hafnium silicates. The difference is that these O atoms are also bonded to Hf atoms, not other Si atoms. Hf is one of the few elements that is more electropositive than Si, so insertion of a Hf ion to form a Hf-O-Si complex would reduce the ionicity in the Si-O bond (compared to one in a Si-O-Si complex). The shift of the Si oxide XPS feature to shallower BE indicates that Hf donates charge to the SiO_2 complexes in the newly formed silicate compound. The BE shift, therefore, corroborates that Hf is able to reduce SiO_2; conversely, Si will be unable to reduce HfO_2, and interfacial SiO_2 formation will be thermodynamically unfavorable.

These results suggest a processing route for production of clean, high-dielectric films that is compatible with present processing technology. Unlike direct deposition of the silicate (as used in previous studies), solid-state reaction would allow the well-developed procedures for producing a high-quality SiO_2 layer with a good Si interface to be retained in the processing. In contrast, the direct deposition of a silicate layer onto bare Si would require that any SiO_2 layer be first removed, exposing the bare surface to the ambient or to the poor vacuum found in sputter deposition tools. Solid-state reaction therefore promises better and less contaminated dielectric-Si interfaces. Also, it is likely our method can be extended to allow deposition of the required Hf metal by chemical vapor deposition (CVD), rather than electron-beam evaporation, further simplifying its implementation.